PATENT

(21) No. of filing report ....158.244 – Paris.
(22) Filing date ....July 8, 1968, at 2:06 pm.
     Date of issuance order....................................May 12, 1969.
(46) Date of publication of descriptive abstract in the
     Official Gazette of Patent Rights ....June 20, 1969 (No. 25).
(51) International classification...............................C 10 g.

(54) **Hydrocarbon reforming process.**

(72) Invention:

(71) Applicant: Company named: TOYO ENGINEERING CORPORATION, residing in Japan.

     Agent: Cabinet Lavoix.

(30) Conventional priority:

(32) (33) (31) *Patent filed in Japan on July 10, 1967, No. 44.268/1967 in the name of the
     applicant.*

This invention concerns a hydrocarbon steam reforming process in order to obtain gasses essentially composed of hydrogen.
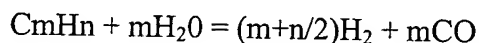
In order to prepare gasses such as those used in the synthesis of ammonia, which are mostly composed of hydrogen, the process of steam reforming of light hydrocarbons has been used extensively.

In the typical steam reforming process, highly diverse feedstocks are used, ranging for example from methane containing one atom of carbon to ethane, to propane and even to heavy naphthas.

These hydrocarbons are used either separately or in mixtures of two or more, in given ratios, or they may be used in a mixture with hydrogen, nitrogen, carbon dioxide, carbon monoxide, etc., in given ratios.

The charging stocks are used in gaseous or liquid form, under an appropriate pressure, and previously heated to an appropriate temperature, if necessary, after the desulfurization.

A charging stock is mixed with steam, or a mixture obtained in this manner, which is then introduced in a tube-in-shell reactor filled with a catalyst consisting essentially of nickel, which causes the hydrocarbon or hydrocarbons used as charging stocks to be reformed by the reaction represented by the following equation:

$$CmHn + mH_2O = (m+n/2)H_2 + mCO$$

This reaction is endothermic and a large quantity of heat is necessary to perform the reaction. In order to meet this requirement, a fuel is burned in the burners mounted on the bottom part or the side wall of the heating furnace, thus heating the tube-in-shell reactor filled with catalyst and providing the latter with sufficient calories to perform the above-mentioned reaction. The by-products of the reaction remain in the form of methane in the produced gas, even if the charging stock is a very heavy hydrocarbon.

As is well known in the industry, the temperature of the reaction must be maintained as high as possible for this endothermic reaction. However, since the tube-in-shell reactor is heated under pressure in the heating furnace, the limit of the mechanical strength of the tube and the limit of the allowable temperature that is controlled by the pressure of the reaction present problems of significant importance.

It is very desirable to use the tube-in-shell reactor at the two limiting values while connecting one with the other.

A reactor that contains several of these tube-in-shell reactors arranged in a heating furnace is named primary reforming furnace, as opposed to the reactor that will be described below. The reaction product exiting the primary reforming furnace is sent to a pressure vessel named secondary reforming furnace, which is filled with a catalyst composed mostly of nickel, like that used in the primary reforming furnace. In the secondary reforming furnace, another reforming reaction is performed after adding a quantity of air appropriate for the load.

For the synthesis of ammonia, the quantity of air to be added is such that it must contain a stoichiometrically sufficient quantity of nitrogen to allow for the synthesis of ammonia. The combustion of the load, with the oxygen contained in the air thus added, raises the temperature of the stream being processed in the secondary reforming furnace. As a result, the methane present in the processed stream exiting the primary reforming furnace is efficiently transformed into hydrogen and carbon monoxide, under optimized equilibrium conditions, at the elevated temperature.

While the processed stream exiting the primary reforming furnace is usually at a temperature of about 300°C, and contains from 7 to 10 % methane (dry gas), the processed stream exiting the secondary reforming furnace is at approximately 1000°C, and the methane content is lowered to about 0.2%, although this content varies a little according to the pressure used for the reaction.

The processed stream that exited the secondary reforming furnace is subjected to a series of purification treatments, that is to transform the carbon monoxide contained in said stream into hydrogen, through a conversion reaction, to eliminate the carbon dioxide contained, and, lastly, to methanize or eliminate the carbon monoxide with the help of a coppery compound. This is how the treatments allow the processed stream to only contain hydrogen, nitrogen and constituents that are not detrimental to the catalyst used in the synthesis of ammonia, that is methane and argon. The purified stream is then loaded, after compression, towards the next stage of the ammonia synthesis process. In this case, gasses such as methane and argon, which are inert in relation to the reaction of ammonia synthesis reaction, accumulate in the ammonia synthesis system. To avoid this accumulation, part of the processed stream is discharged from the ammonia synthesis system. At the same time, however, precious hydrogen and nitrogen are also

partially discharged as they are carried away by the stream thus discharged. That is the only drawback of the final stage of purification of the ammonia synthesis gas by methanization or elimination of carbon monoxide with a solution of coppery compound. Thus, an increase in the methane content of the stream exiting the secondary reforming furnace inevitably increases the quantity of the processed stream that is purged from the ammonia synthesis system. For this reason, it is important that the methane content of the processed stream exiting the secondary reforming furnace be maintained as low as possible.

As is well known, an increase in the reforming pressure can significantly increase the overall economical interest of the preparation stages. The reason being that the benefit arising from the lower energy requirements in order to compress the purified gas intended for the synthesis of ammonia, at the operating pressure for the ammonia synthesis process, more than offsets the inconvenience of the increased energy requirements due to the increase of the reforming pressure, in order to compress the charging stock as well as the air, etc., which are introduced into the secondary reforming furnace. Consequently, it is generally possible to improve the economic aspect of the production stages by using a higher reforming pressure.

However, a significant restriction must be imposed on the deliberate increase of the reforming pressure according to the above-mentioned principle. On account of the mechanical strength of the tube-in-shell reactor, which is an essential determining factor in this case, the temperature of the tube-in-shell reactor walls must be decreased in order to increase the reforming pressure. If the reforming pressure is increased and the reaction temperature is decreased in this manner in the primary reforming furnace, the reaction temperature in the secondary reforming furnace will naturally decrease and, since the reforming reaction is endothermic, the quantity of residual methane in the processed stream exiting this last furnace will increase. This could have a decisive harmful effect on the overall economic characteristics of the preparation process, as noted previously.

In order to solve this tricky technical problem, it was proposed to pre-heat the air introduced in the secondary reforming furnace. The pre-heating of the air made it possible to maintain the processed stream exiting the secondary reforming furnace at a relatively constant temperature of about 1000°C, and to slightly decrease the temperature of the processed stream exiting the primary reforming furnace, resulting in an increase of the reforming pressure. In other words, the process designed as described above made it possible to inhibit the increase in

residual methane concentration, increase the reforming pressure and thus improve the economics in terms of the entire process.

However, the increase of the reforming pressure through the process based on the foregoing is limited to about 30 to 40 atmospheres. The attempts made to further increase the reforming pressure are again subject to the above-mentioned technical limitations, because the quantity of heat supplied to the processed stream by the pre-heated air is limited by the low heating power of the air itself.

Between the steam reforming process and the pressure gasification process with partial oxidation, there is yet a significant technical gap in that the reaction pressure, in the last process, was increased to about 80 to 100 atmospheres or more. Thus, in order to achieve a better overall economy in the preparation stages, it has become apparent in the steam reforming process that there is a need for a more advance technique.

The applicant discovered unexpectedly, after a careful analysis of the conventional steam reforming process, that the above-mentioned technical problem could be resolved with the help of extremely simplified means, and the process is thus successfully improved.

The purpose of this invention is a hydrocarbon steam reforming process at high pressure, according to which a primary reforming reaction is performed through the catalytic reaction of a mixture of hydrocarbon(s) and steam, with the help of external heating; a secondary reforming reaction is performed by adding air to the processed stream originating from the primary reforming reaction zone, and the processed stream is made to react catalytically with the help of the heat produced in the system by combustion with the oxygen contained in the air, which process is characterized by the fact that the processed stream is pre-heated in the primary reforming reaction zone by heat exchange with the processed stream in the secondary reforming reaction zone, and is introduced in the secondary reforming zone where the steam reforming reaction is performed.

Other advantages and characteristics of the invention will appear in the course of the following description. In the attached drawing, which is provided only as an example,

Figure 1 is a diagram of a device for the implementation of the steam reforming process according to the invention, and

Figure 2 is a vertical sectional view showing a heat exchanger that can be used in the process according to the invention.

By referring to Figure 1, a mixture of hydrocarbon used as charging stock, and steam exiting from pipe 1 is introduced in tube-in-shell reactors 2 lined with beds of catalyst 3.

The tube-in-shell reactors 2 are heated by the combustion of fuel introduced by a pipe 4 into the heating furnace 5, which causes a primary reforming reaction to continue within the catalyst beds 3.

A processed stream coming from the primary reforming furnace, having flowed through the catalyst beds 3, is introduced by a pipe 6 into a heat exchanger 7 where it is heated, and it is loaded in the top part of a secondary reforming furnace 8.

In the conventional process, the processed stream is not introduced in this heat exchanger 7, but is directly loaded into the top part of the secondary reforming furnace 8.

Compressed air, supplied by a pipe 9, is pre-heated by a pre-heating device 10 installed in the discharge stack of the heating furnace 5, up to a temperature of about 500°C, or, in certain cases, ----------------, about 800°C, and is loaded by a pipe 11 in the top part of the secondary reforming furnace 8.

The processed stream coming from the primary reforming furnace, heated by the heat exchanger 7, and the air loaded by the pipe 11 are mixed in the top part of the secondary reforming furnace 8, and the mixture is sent to a catalyst bed 12.

In the latter, a secondary reforming reaction occurs thanks to the heat released by the combustion with the oxygen of the air supplied by the pipe 11.

Once that the secondary reforming reaction is completed, the processed stream is sent through a pipe 13, while reheating the heat exchanger 7 during its run, toward a subsequent stage of ammonia synthesis (not shown).

The presence of the heat exchanger 7 makes it possible to decrease the temperature of the processed stream from the primary reforming furnace in the pipe 6, while retaining a high reaction temperature in the catalyst bed 12. Since the drop in the temperature of the processed stream coming from the primary furnace is made possible in this manner, the heat that the tube-in-shell reactors must withstand can be decreased and their resistance to the pressure can consequently be improved. This, in turn, makes it possible to increase the pressure for the steam reforming and brings about an overall reduction of the energy requirements for the preparation of ammonia.

Figure 2 shows a type of secondary reforming furnace used in the process according to the invention.

The processed stream coming from the primary reforming furnace is introduced in a spiral-tube heat exchanger 7 through an inlet port 14 located on the bottom part of a secondary reforming furnace 8.

In the heat exchanger 7, the processed stream coming from the primary reforming furnace is heated by the processed stream which just exited from the catalyst bed 12 of the secondary reforming furnace 8. The heat exchange is performed through the tubular wall made of metal or other material of the heat exchanger 7. The mechanical stress to which the tubular walls are subjected is quite insignificant.

This mechanical stress is produced, in large part, by the difference between the pressure of the processed stream coming from the primary reforming furnace and that of the processed stream exiting the catalyst bed of the secondary reforming furnace, such pressure difference depending mostly upon the catalyst bed 12, which is usually not greater than 0.5 kg/cm2.

Consequently, all that is required is for the tubular walls of the heat exchanger 7 to withstand this insignificant mechanical stress. This simplifies the construction of the heat exchanger 7, and the simplification thus accomplished may be considered as an additional benefit of the invention.

The heat exchanger 7 may be made of metal or another material such as, for example, ceramic, as mentioned above. Normally, an ordinary steel alloyed with nickel and chromium is well suited.

Although the heat exchanger 7 could be of any known type, a spiral-tube type heat exchanger like the one shown in Figure 2 is preferred.

The heat exchanger 7 is preferably divided into two (or more than two) small diameter tubes, in order to obtain a larger heat exchange surface within a given space.

Furthermore, fins (not shown) are advantageously formed on the external face of the exchanger in order to increase the overall heat exchange surface.

To increase the heat exchange, it is desirable to reduce the inside diameter of the bottom part of the secondary reforming furnace that contains the heat exchanger 7, or to make sure that it is the same as that of the top part where the catalyst bed 12 is contained, and to provide a baffle at the same time as the heat exchanger in the bottom part of the secondary reforming furnace,

because this device is useful to increase the flow rate of gas on the high temperature side, that is the flow rate of the processed stream that exits the catalyst bed 12.

The processed stream, after having passed through the heat exchanger 7 and being heated, is sent through a riser 15 toward the top part of the secondary reforming furnace, and discharged through a port 16 into the top part of the furnace. Furthermore, pre-heated compressed air is introduced in the secondary reforming furnace by the pipe 11. The air mixes with the processed stream coming from the port 16, and the overall stream flows down through the catalyst bed 12, which makes it possible to perform the secondary reforming reaction.

The hot processed stream coming from the catalyst bed 12 provides its own heat, through the heat exchanger 7, to the processed stream loaded toward the secondary reaction furnace, and is then discharged through an outlet port 17, toward the following stage of ammonia synthesis (not shown).

Although Figures 1 and 2 show the heat exchanger 7 installed within the secondary reforming furnace, the secondary reforming furnace can also be connected to an independent pressure vessel, in which a heat exchanger 7 can be provided. In this last case, the heat exchanger can also be designed ideally as such, without having to take into consideration, from a practical standpoint, its relationship to the layout of the secondary reforming furnace.

The following example is given for the purpose of illustrating the invention.

While reforming pressures of 30 to 40 atmospheres were considered maximum until now, the use of pressures as high as 50 to 60 atmospheres has become possible thanks to the process according to the invention. Even higher reforming pressures could be used by using tube-in-shell reactors with smaller diameters than the tube-in-shell reactors used until now.

The example shows the results obtained by applying the process according to the invention to an ammonia synthesis facility with a production capacity of 660 tons per day.

The hydrocarbon used as a charging stock is natural gas consisting mainly of methane.

The hydrocarbon used as charging stock is mixed with steam according to a mole ratio of about 1/3.5, and the mixture is run through heat resisting tube-in-shell reactors with an inside diameter of 100 mm, each filled with a catalyst and placed in an furnace.

The processed stream exits the tube-in-shell reactors at a pressure of 50 atmospheres.

The stream is maintained at this pressure at a temperature of 750°C in order to take into account the creep of the pipes.

The stream is heated to 900°C by the stream coming from a secondary reforming furnace, with the help of a heat exchanger, and is introduced into the top part of the secondary reforming furnace, at the same time as the compressed air that has been pre-heated to 700°C.

Once that the oxygen contained in the compressed air is consumed by combustion, the processed stream is run through the catalyst bed, into the secondary reforming furnace.

The stream exiting the catalyst bed of the secondary reforming furnace is at a temperature of 1013°C, and its methane concentration is about 0.2%.

Since the top limit of the reforming pressure used is typically between 30 and 40 atmospheres, the reforming pressure according to the invention is increased by about 10 to 20 atmospheres, as demonstrated by this example.

The power consumption saved on account of the reforming pressure increase, for the preparation of ammonia, is about 2000 KWh/h when the natural gas used as charging stock is loaded at a pressure lower than 55 atmospheres, or about 1500 KWh/h when the natural gas is loaded at a pressure equal to or less than 35 atmospheres.

The savings achieved in the power consumption represents about 6% and 4.5%, respectively, of the total power requirements of the conventional process of ammonia preparation.

There are other benefits. In the devices relating to the conventional process, a boiler that uses waste heat is mounted immediately behind the secondary reforming furnace in order to recover the heat of the processed stream in the form of steam. However, since the processed stream is at high temperature and pressure, hydrogen corrosion tends to occur, which is a source of constant and serious problems for the design and maintenance of the facility.

Furthermore, the heat exchanger designed according to the process of the invention lowers the temperature of the processed stream to such a degree that, although a boiler using waste heat or a similar device is installed behind the secondary reforming furnace, the design and maintenance are highly simplified, and this contributes significantly to the stability of the operations and to the improved productivity of the facility as a whole.

It shall be noted that the benefits provided by this invention not only result in the higher reforming pressure, but also in that, when the invention process is implemented under a typical reforming pressure, the thickness of the walls of the tube-in-shell reactors can be reduced, and

furthermore, it becomes possible to use smaller reforming furnaces or smaller boilers that use waste heat.

Of course, the invention is not limited to the implementation modes represented and described herein, which were only given as examples.

ABSTRACT

The purpose of this invention is a hydrocarbon steam reforming process, according to which a primary reforming reaction is performed through the catalytic reaction of a mixture of hydrocarbon(s) and steam, with the help of external heating; a secondary reforming reaction is performed by adding air to the processed stream originating from the primary reforming reaction zone, and by causing the processed stream to react catalytically with the help of the heat produced in the reaction zone by combustion with the oxygen contained in the air, which process is characterized by the fact that the stream coming from the primary reforming zone is pre-heated in a heat exchanger by a processed stream coming from the secondary reforming zone, and is then introduced in the secondary reforming zone.